

Kramers rate theory of bound-state dissociation at low and high densities

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Calculating the microscopic dissociation rate of a bound state, such as a classical diatomic molecule, has been difficult so far. The problem was that standard theories require an energy barrier over which the bound particle (or state) escapes into the preferred low-energy state. This is not the case when the long-range repulsion responsible for the barrier is either absent or screened (as in Cooper pairs, ionized plasma, or biomolecular complexes). We solve this classical problem by accounting for entropic memory at the microscopic level. The theory predicts dissociation rates for arbitrary potentials and is successfully tested on the example of plasma, where it yields an estimate of ionization in the core of Sun in excellent agreement with experiments. In biology, the new theory accounts for crowding in receptor-ligand kinetics and protein aggregation.

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The rate of escape of a classical particle over an energy barrier is a well-posed problem as long as the potential energy features a barrier or transition-state that has to be crossed [1]. This is the classical Kramers problem [2], Fig. 1(a), that has served very well in many areas of science. However, the escape-rate problem is known to be ill-defined when the particle is trapped in a potential well which is the only point of minimum in the potential profile (which then either diverges or reaches asymptotes along the coordinated axis) [1]. The latter case is typically exemplified by two noble gas atoms bonded by van der Waals forces such that each atom is trapped in the Lennard-Jones potential well. The same applies to many other sorts of bound states (e.g. diatomic molecules [3, 4], deuterons [5], Cooper pairs [6], nuclear neutrons [5], etc.) in the absence of long-range repulsion, Fig. 1(d)-(f). In all such cases, the Kramers and transition-state theories cannot be applied because the flux driving the particle out of the well cannot be defined, and in fact not even an energy barrier to be crossed can be identified. This is in contrast to many other situations where the competing long-range repulsion gives rise to a well-defined barrier, Fig. 1(a)-(c). In spite of this theoretical difference, in all these systems the observed time of escape is still finite and a theoretical estimate is desirable for many applications. This is a long-standing and well-known problem [1]. The common remedy to this difficulty, so far, was to employ fictitious absorbing boundaries or long-range repulsions to artificially create a barrier or transition-state which would allow one to apply the Kramers theory for the escape rate over such a barrier [7]. This procedure has the shortcoming that the resulting barrier or transition-state is completely arbitrary, and so are the results for the calculated dissociation rates.

Inspired by Peierls [8], here we propose a solution to this problem by considering the role of entropy in the escape process. It is known that entropic contributions can influence kinetics in several contexts [10]. As an example we recall the problem of the equilibrium flux through bottlenecks with a cross-section fluctuating in time studied by Zwanzig [11], where even in the absence of energy

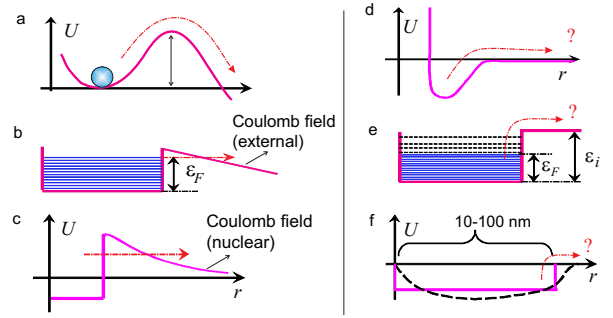


FIG. 1: Examples of situations where the dissociation problem is well defined (a-c) and where it is not (d-f). (a) The Kramers escape problem [2]. (b) Field-emission of electrons [3], where the external electric field gives rise to a well-defined barrier through which the electron can escape or tunnel away. (c) The escape of α -particles from atomic nuclei [3], where the repulsion is between positive charges. (d) The internuclear potential of a diatomic molecule or molecular complex [9]. (e) Potential of electrons at metal surfaces (thermionic effect) or by neutrons evaporating from hot nuclei [5]. (f) The attractive potential between the two electrons of a Cooper pair in real-space [6].

barriers due to conservative potentials, the passage time is controlled by entropic barriers due to the fluctuations. However, the question about the fundamental mechanism by which entropy comes into play has remained largely unanswered and an analytical framework of general applicability is lacking. Here we show how entropy drives the flux responsible for dissociating the bound states in the absence of stabilizing barriers and analytically calculate the microscopic dissociation rate of classical bound states. The generic theory is validated by showing that it is able to recover the classical Saha ionization degree in the dilute limit. Further, our approach is fully microscopic, which allows us time to include the density effects in the recombination process.

Effective pair-interaction energy for dissociation. We start with two thermal particles bonded by an attractive interaction where it is evident that upon moving apart

from one another along the radial coordinate the two particles will be less favored in terms of potential energy but they will gain a larger free volume, and hence more entropy. Furthermore, one should remark that the “pair-interaction energy $w(r)$ ” between two molecules or particles separated by a distance r is usually identified by the force f acting between the two particles via $f = -dw(r)/dr$; hence one finds the work that can be done by the force. This means that $w(r)$ is actually the *free energy* or the available energy for the two-particle system [9] because the local collisional physics allows us to define an entropy in addition to the potential energy. Rigorously, the effective pair-potential for the two-particle system is thus given by: $w(r) = U(r) - T\Delta S(r)$, where U is the conservative potential energy of interaction between the two particles and ΔS is the mixing entropy of the system. Let us interpret the dissociation coordinate r as a time-averaged position where the average is taken over a time $t > \tau_c$ where τ_c is the collision time-scale between the two bound particles. Then, the contact force f_c due to collisions between the two particles constrained to remain at close contact over a finite amount of time obeys the scaling relation [14]: $f_c \sim k_B T/r$. For two hard-spheres constrained into a small portion of space where they collide repeatedly with each other, the contact force can be integrated to give an associated pair-interaction free energy which is related to the entropy of the two-particle system: $T\Delta S(r) \sim k_B T \ln(r/R)$ where we chose the integration constant equal to $-\ln R$. In the presence of a conservative interaction $U(r)$ the total interaction force is thus given by $f = f_c - (dU(r)/dr)$ and the corresponding total effective pair-interaction is given by $w(r) \simeq U(r) - k_B T \ln(r/R)$. A more precise form for this effective pair interaction, including prefactors, can be derived using a different method, which makes use of the Onsager excluded volume theory [13]. With this method one obtains:

$$\Delta S = k_B \left(2 \ln \frac{V_1}{2v_p} + \frac{u}{2v_p} \right) = k_B \left(2 \ln \frac{r^3}{2R^3} + 4 \right), \quad (1)$$

where $V_1(r) = 4\pi r^3/3$, $u = 4\pi(2R)^3/3$, and v_p is the volume of one particle. This equation expresses that fact that upon moving the particles apart along the outward radial coordinate r there is a net entropy gain which arises from the increased number of degrees of freedom explored by the particles. Hence the interaction energy can be rewritten as

$$w(r) = U(r) - k_B T \left(6 \ln \frac{r}{R} + 4 - 2 \ln 2 \right). \quad (2)$$

Based on these considerations, the effective pair-interaction potential given by Eq. (2) is coarse-grained in the sense that is valid only for particles that have been kept at close distance for a time $t \gg \tau_c$ [14]. As such, Eq. (2) can be applied to the dissociation of pairs of particles which are bonded by some attractive potential $U(r)$. On the other hand, for two particles which approach each other from far apart, their mutual interaction prior to

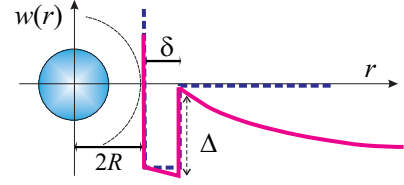


FIG. 2: Schematic of the rectangular-well potential around a particle of radius R used for $U(r)$ in the derivation, shown by the dashed line. It is the effective potential (free energy) $w(r)$, solid line, with its entropic correction making the higher separation r favorable, that affects the dissociation of the bound state.

colliding happens on a time scale $t \leq \tau_c$, i.e. they cannot explore their mutual excluded volume. Therefore for the recombination process there is no entropic effect and $w(r) \rightarrow U(r)$. This can be understood by recalling that entropy in classical systems is ultimately related to collisions which are important in the bound-state where the particles preserve “memory” of each other [15] over the life-time of the bound state and this makes their configurational entropy depend on their separation. In the recombination process, however, since the conservative potentials U that we consider here do not have a barrier, the recombination of diffusive particles is diffusion-limited and occurs at the very first collision event between the two particles. Therefore, no entropic contribution applies to recombination processes of this kind where the recombination rate is uniquely determined by the diffusion process in the field of the conservative potential U . In the following we will use these arguments to derive microscopic dissociation and recombination rates with the tools of statistical mechanics.

Dissociation rate. Without loss of generality, but to simplify the algebra and emphasize the qualitative point, let $U(r)$ in Eq. (2) be a rectangular-well attractive potential, of range δ (Fig. 2, dashed line), so that two particles constrained within a distance $r = 2R + \delta$. Due to the entropy contribution, $w(r)$ from Eq. (2) decreases logarithmically at large distances, while having little effect on the proximity well. Such an effective potential (free energy) features a now well-defined barrier over which the bound particle can escape. Using the Kramers escape theory for the 3D spherically-symmetric problem [1], the escape time, i.e. the reciprocal of the escape rate κ , is given by

$$\frac{1}{\kappa_{diss}} = \int_{2R}^{r_{min}} \frac{e^{-w(r)/k_B T}}{D} r^2 dr \int_{r_{min}}^C \frac{e^{w(r)/k_B T}}{r^2} dr. \quad (3)$$

The upper limit $C \gg R + \delta$ is some arbitrary point far away along the radial axis and $r_{min} = 2R + \delta$ is the minimum of the effective potential $w(r)$; D is the diffusion coefficient for this problem. Using Eq. (2) in Eq. (3) the integrals can be evaluated analytically which gives the

compact expression for the dissociation rate:

$$\kappa_{diss} = 63D \left[\frac{(2R + \delta)^7}{(2R + \delta)^9 - (2R)^9} \right] e^{-\Delta/k_B T}. \quad (4)$$

The escape rate is directly proportional to the diffusion coefficient, as in the classical Kramers theory. It is important that this dissociation rate decreases with the increasing width of the attractive well, δ : this is a natural reflection of the fact that the effective frequency of the particle in the potential well (related to the ‘rate of attempts’ to overcome the barrier) increases as $\delta \rightarrow 0$. The height of the effective energy barrier in the exponential thermal-activation term, is given by $\Delta/k_B T$, that is, by the depth of the original square well potential. This explains why a number of *ad hoc* theories produce results that are qualitatively valid; the crux here is in the detail.

Recombination rate. Once the dissociation of the bound state occurs, i.e. the bound particle has crossed the barrier in the effective potential of Fig. 2, the two particles move apart. For a dilute thermal system, the mechanism of recombination back into the bound state is controlled by the diffusive transport. With interacting particles, the recombination rate is determined by solving the stationary Smoluchowski (diffusion) equation in the field of force due to the interaction. For the attractive square-well case the solution is:

$$\kappa_{rec} = \frac{4\pi D}{e^{-\Delta/k_B T} \left(\frac{1}{2R} - \frac{1}{2R+\delta} \right) + \frac{1}{2R+\delta}} \quad (5)$$

Since δ is finite and for $\Delta/k_B T > 1$, the first term in the denominator is small compared to the second term due to the exponential factor, and thus we obtain:

$$\kappa_{rec} \approx 4\pi D(2R + \delta). \quad (6)$$

This result can be extended to denser fluids using a generalized diffusion coefficient given by $D(n) = (D/k_B T) d\Pi(n)/dn$ where Π is the osmotic pressure of the fluid medium and $n \equiv N/V$ is the average number density of diffusing particles [17]. Using this $D(n)$ in the above solution to the Smoluchowski diffusion equation, one obtains the generalization of the recombination rate for dense and crowded systems [17]: $\kappa_{rec} \approx 4\pi D(2R + \delta)\Pi(n)/nk_B T$. The correction can be easily evaluated once the equation of state (EOS) of the fluid is known. In the simplest non-ideal case one can express the EOS in terms of the virial expansion [18]. For model hard-sphere fluids one can use the Carnahan-Starling EOS [19]: $\Pi/nk_B T \equiv Z(\phi) = (1 + \phi + \phi^2 - \phi^3)/(1 - \phi)^3$, where ϕ is the fraction of occupied volume in the system, e.g. $\phi = (4\pi/3)R^3 n$. This leads to the recombination-rate coefficient $\kappa_{rec} = 4\pi D(2R + \delta)Z(\phi)$, which would be relevant for a crowded environment. For a dilute solution of biomolecules which bind to form complexes (e.g. receptor-ligand binding) in a sea of other particles of similar size with which they interact by steric repulsion, this leads to recombination rates several times larger than the

Smoluchowski estimate. We remark that for $\phi \gtrsim 0.40$, it is no longer safe to neglect entropic effects on recombination, due to the short-range liquid-like structuring (inhomogeneous local density) around the reactants which cause the incoming particle to collide with an increasing amount of crowders before colliding with the second reactant. This clearly leads to an entropic repulsion upon recombination, as discussed in [17]. These considerations fix the upper validity limit of our theory to $\phi \simeq 0.45$. Extension to glassy systems is non-trivial and will be the object of future work.

If the dense fluid is made of charged particles, such as in high-density plasmas, then the transport is no longer diffusive but drift-controlled. In this case the oppositely charged particles attract each other via the Coulomb force $\sim (Ze)^2/r^2$, where Ze is the electric charge of the particles. The crossover from diffusion-controlled to drift-controlled transport typically happens when $n[(Ze)^2/k_B T]\sigma \gg 1$, where σ is the collision cross-section. In this case the total current of oppositely-charged particles entering the interaction volume is given by: $4\pi r^2 v_d n$, where $v_d = (Ze/r^2)(\mu_- + \mu_+)$ is the drift velocity in the Coulomb attraction field of approaching particles and μ the electrical mobility. The electron-ion recombination-coefficient for dense plasmas is thus given by $\kappa_{rec} \approx 4\pi e\mu_-$, assuming that the electron mobility μ_- is much greater than the ion mobility and $Z = 1$. This is a well-known result from the kinetic theory of plasmas [20].

Dissociation equilibrium. The equilibrium of association and dissociation reactions is of extreme importance for *in vivo* physiological processes, e.g. enzymatic activity based on receptor-ligand complexes or protein aggregation [21, 22]. We will give a treatment of the general case of two classical particles bound by an attractive potential which can be directly applied to biomolecules. The net attractive potential $U(r)$ is of the kind of Fig. 1(d). Given these conditions, the chemical equilibrium constant K for the dissociation-recombination process $B + C \rightleftharpoons BC$ is given by the law of mass action as

$$K = \frac{\kappa_{diss}}{\kappa_{rec}} = \frac{n_B n_C}{n_{BC}} = \frac{N_B N_C}{N_{BC}} \frac{1}{V}. \quad (7)$$

If $N_0 = N_{BC} + N_B = N_{BC} + N_C$ is the total number of each species present in the system, the total number of particles, both bound and dissociated, is given by $N = N_0(1 + \alpha)$, where $\alpha = N_B/N_0 = N_C/N_0$ is the ‘degree of dissociation’ [24]. The relations for the molar fractions of the various species follow at once: $N_B/N_0 = \alpha/(1 + \alpha)$ and $N_{BC}/N_0 = (1 - \alpha)/(1 + \alpha)$.

Using Eq. (4) and the high-density extended Smoluchowski rate for κ_{diss} and κ_{rec} , respectively, this leads to the following expression for the dissociation degree in equilibrium:

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{63}{4\pi} \frac{(2R + \delta)^6}{(2R + \delta)^9 - (2R)^9} \frac{e^{-\Delta/k_B T}}{nZ(\phi)}. \quad (8)$$

In the limit of long-range attraction, $\delta \gg 2R$, this simplifies further and we get the following expression for the degree of dissociation α :

$$\alpha \approx \left[1 + (4\pi/63)n_Z(\phi)\delta^3 e^{\Delta/k_B T} \right]^{-1/2}. \quad (9)$$

In biological systems one often encounters situations where the interaction range can be significant, such as in the ubiquitous case of hydrophobic attraction [25]. Equation (9) shows that the dissociation degree in cases of biological relevance can have a sensitive dependence upon the interaction range δ , which has been neglected in previous theories. Furthermore, Eq. (9) takes into account the enhanced recombination in crowded systems. In the opposite limit of short-range attraction (sticky or adhesive particles [26]), $\delta \ll 2R$, one obtains:

$$\alpha \approx \left[1 + 7.2n_Z(\phi)R^2\delta e^{\Delta/k_B T} \right]^{-1/2} \quad (10)$$

with a much weaker dependence on δ . Finally, we should remark that in the above treatment we assumed $n_B = n_C$, which describes dissociation and ionization kinetics. In receptor-ligand kinetics, however, the concentration of ligands normally overwhelms the concentration of receptors, i.e. $n_C \gg n_B$. Since we derived *intrinsic* rates, we can apply our theory to any kind of kinetics, including the pseudo-first-order situation $n_C \gg n_B$. In this limit, the kinetics is of the Langmuir type [23]: $\theta = Kn_C/(1 + Kn_C)$, where $\theta = N_{BC}/(N_B + N_{BC})$, and K is still given by Eq. (7) with the rates for dissociation and association derived here.

Ionization equilibrium in plasmas. We can further test this theory by addressing the problem of the thermal dissociation of atoms (ionization). This problem was famously addressed in the 1920's by Saha [24] by combining the statistical mechanics of the ideal gas with the chemical equilibrium (detailed balance) assumption. By considering the chemical equilibrium of the ionization reaction $A \rightleftharpoons I^+ + e^-$, the chemical equilibrium constant of the reaction is given by the same expression as Eq. (7). In the dilute limit, Eq. (6) for κ_{rec} applies, and using Eq. (4) for κ_{diss} we obtain

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{63}{4\pi} \frac{V}{Nv} e^{-\Delta/k_B T} \quad (11)$$

where $N = N_A + N_{I^+} + N_{e^-}$. The interaction volume, as we have shown above, is given by $v \equiv [(2R + \delta)^9 - (2R)^9]/(2R + \delta)^6$. The extension of the radial probability amplitude for a bound electron, λ_{e^-} , is approximately given by the width of the attractive well, and therefore we take $\delta \simeq \lambda_{e^-}$. In the classical approximation valid at high temperatures, λ_{e^-} is the thermal de Broglie wavelength, $\lambda_{e^-} = \hbar/\sqrt{m_e k_B T/2\pi}$. Furthermore, one has $\lambda_{e^-} \gg \lambda_{I^+}$, such that $v \equiv [(\lambda_{I^+} + \lambda_{e^-})^9 - (\lambda_{I^+})^9]/(\lambda_{I^+} + \lambda_{e^-})^6 \simeq \lambda_{e^-}^3$, i.e. the same limit as used in Eq. (9). With this replacement in Eq. (11), our theory for a dilute plasma where free diffusion is the main transport

mechanism correctly reduces to the Saha equation [24], apart from a numerical pre-factor of order unity. This result demonstrates the validity of the proposed calculation scheme.

The Saha equation works well for dilute plasmas, but it breaks down in the core of the stars [27]. In fact, the opacity in the interior of stars (such as the Sun) is extremely low for that high density, and this implies that the interior is formed by completely ionized matter with $\alpha \simeq 1$. Evaluating the Saha equation at the typical conditions of the stellar interiors gives $\alpha \simeq 0.7 - 0.8$ that is incompatible with the observed vanishing opacity. We can now extend the theory to the high-density regime because we can include transport effects, that are important at high density, via the recombination rate which enters in our model. Using the recombination rate for high-density plasmas given by $\kappa_{rec} \approx 4\pi e\mu_-$ in the equilibrium constant for atomic dissociation $K = \kappa_{diss}/\kappa_{rec}$, we obtain

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{63}{4\pi} \frac{k_B T V}{e^2 \lambda_{e^-}^2 N} e^{-\Delta/k_B T} \quad (12)$$

where we used the Einstein relation $eD/k_B T = \mu$ for the single-electron ionization, $Z = 1$, and continued using $\delta \simeq \lambda_{e^-}$ for the bound state of electron. Let us calculate α for the conditions corresponding to the core of the Sun, i.e. $T = 10^7 K$, $N/V = 10^{26} \text{cm}^{-3}$, and assume pure hydrogen. The Saha equation gives $\alpha \simeq 0.79$, whereas from Eq. (12) we obtain a much more realistic $\alpha \simeq 0.99$. Clearly, Eq. (12) is in excellent agreement with the experimental data indicating fully-ionized plasma conditions in the core of the Sun [28].

To conclude, we have proposed a theoretical scheme that allows one to calculate the intrinsic dissociation rate of bound states with purely attractive potentials, something so far possible only for potentials that feature long-range repulsion competing with attraction. In all the other cases, including dissociation of neutral atoms, molecules, Cooper pairs, molecular complexes, this was not possible and required various *ad hoc* assumptions. We validated our theory for its predictions of the ionization degree of hydrogen-like atoms, a problem relevant in several branches of astrophysics. Our theory correctly reproduces the Saha formula at steady-state in the ideal-gas limit. Further, it can be easily extended to deal with the high-density limits. In fact it predicts full ionization in the core of stars, thus dramatically improving over the Saha equation that predicts partial ionization. Further applications are in biology where it allows one to calculate dissociation equilibria of receptor-ligand or protein complexes in presence of cellular crowding.

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